# The Mass-transfer Rate through the Liquid-Liquid Interface. VII. Diffusion through a Spherical Interface Involving the Adsorption-Desorption Process

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A theoretical formula for the transfer rate of a solute through a spherical interface has been proposed, considering the adsorption-desorption process and the variation in the amount of adsorption. Computational results indicate that, in the usual particle-diameter (radius $<1$ mm), the diffusion coefficient has practically no relation to the transfer rate in the case of a significant interfacial resistance, such as is observed in the transfer of fatty acids. The concentrations of butylamine in the aqueous, continuous phase in a stirred extraction vessel have been predicted.

In the treatment of mass transfer through oil–water interfaces, the adsorption-desorption process on the interface has usually been disregarded in chemical engineering practice; that is, the two concentrations in both phases next to the interface have been assumed to be in equilibrium. The ground of this disregard of the process is supposedly that the transfer rate has not physically, but rather formally been treated in terms of the "mass-transfer coefficient;" also, that the resistance encountered when a solute molecule transfers through an oil–water interface has been generally considered to be negligible.

Some authors have studied and investigated, however, about the magnitudes of the interfacial resistances; their results[1–7] indicate that usually the resistance is fairly significant. A theoretical formula[8] of mass-transfer rates was derived in the case of linear diffusion through the plane interface in a finite composite medium, considering the adsorption-desorption process on the interface and also the variation in the amount of adsorption; the analytical results[7] from the observed transfer rates of propylamine and butylamine through the water–benzene interface using the derived formula showed that the activation free energies of desorption of the solutes from the interface were about 18 kcal[†]/mol at 50 °C, which agreed with the results[4–6] obtained by other procedures from the transfer rates of fatty acids through oil–water interfaces.

In an actual and effective operation of the technical extraction of substances, the oil–water system is composed of a dispersed phase and a continuous phase in a stirred vessel or in a dropping tower; the role of the interfacial process of transfer may become important as the liquid-drop goes to smaller sizes.

Below we shall treat theoretically, from the above point of view, the mass-transfer rates through a spherical interface involving the adsorption-desorption process and the variation in the amount of adsorption.[9]

## Theory

Modified Fick's diffusion equations for a composite spherical system[10] are defined by

$$\partial u_1/\partial t = D_1(\partial^2 u_1/\partial r^2), \quad 0 \leq r < R_1, \quad t > 0; \qquad (1)$$

$$\partial u_2/\partial t = D_2(\partial^2 u_2/\partial r^2), \quad R_1 < r < R_2, \quad t > 0, \qquad (2)$$

where $u_1$ and $u_2$ are related to $c_i$, $i=1$ or 2, as $u_i \equiv rc_i$; here, $c_i$ is the local concentration of the solute in Phase $i$; $D_1$ and $D_2$ are the diffusion coefficients; $r$ is the distance from the center of the composite (concentric) sphere; $t$ is the time, and $R_1$ and $R_2$ are constants.

The boundary conditions are represented by

$$-D_1\{(\partial u_1/\partial r)/r-(u_1/r^2)\} + D_2\{(\partial u_2/\partial r)/r-(u_2/r^2)\} = \Gamma_\infty(\mathrm{d}\theta/\mathrm{d}t), \quad r = R_1, \quad t > 0; \qquad (3)$$

$$-D_1\{(\partial u_1/\partial r)/r-(u_1/r^2)\} = k_{\mathrm{a1}}(1-\theta)u_1/r-k_{\mathrm{d1}}\theta, \quad r = R_1, \quad t > 0; \qquad (4)$$

$$D_2\{(\partial u_2/\partial r)/r-(u_2/r^2)\} = k_{\mathrm{a2}}(1-\theta)u_2/r-k_{\mathrm{d2}}\theta, \quad r = R_1, \quad t > 0; \qquad (5)$$

$$u_1 = 0, \quad r = 0, \quad t > 0; \qquad (6)$$

$$u_2 = R_2 c_{2\omega}, \quad r = R_2, \quad t > 0, \qquad (7)$$

where $\Gamma_\infty$ is the saturated value of the amount of adsorption per unit of area of the interface; $\theta$ is the fraction of the total interface occupied by adsorbed molecules; $k_{\mathrm{a1}}$ and $k_{\mathrm{a2}}$ are the rate constants of adsorption to the interface from Phase 1 and Phase 2 respectively; $k_{\mathrm{d1}}$ and $k_{\mathrm{d2}}$ are the rate constants of desorption from the interface to Phase 1 and Phase 2 respectively, and $c_{2\omega}$ is a constant. Equation 3 relates the variation in the amount of adsorption to the fluxes, while Eqs. 4 and 5 give the relation between the adsorption-desorption mechanism and the fluxes.

The initial conditions are assumed to be

$$u_1 = rc_{10}, \quad 0 \leq r < R_1, \quad t = 0; \qquad (8)$$

$$u_2 = rc_{2\omega}, \quad R_1 < r \leq R_2, \quad t = 0; \qquad (9)$$

$$\theta = \theta_0, \quad t = 0, \qquad (10)$$

where $c_{10}$ and $\theta_0$ are constants as well as $c_{2\omega}$.

Equations 1—10 are to be solved by means of the Laplace transformation; in an extreme case, $(R_2-R_1) \to 0$ (then $R_1 = R_2 = R$), considering a dynamic system such as in a stirred vessel, the solution may be expressed as

$$c_{1,i} = (k_{\mathrm{a1}}k_{\mathrm{d2}})^{-1}k_{\mathrm{a2}}k_{\mathrm{d1}}c_{2\omega} + (2/r)\sum_{n=1}^{\infty}\boldsymbol{D}^{-1}\xi_i \sin(r\alpha_n) \times \exp(-D_1\alpha_n{}^2 t); \qquad (11)$$

$$\theta_{,i} = (k_{\mathrm{a2}}/k_{\mathrm{d2}})c_{2\omega} + 2(\Gamma_\infty R)^{-1}\sum_{n=1}^{\infty}\boldsymbol{D}^{-1}\{\zeta_{1,i}\sin(R\alpha_n) + \zeta_{2,i}\cos(R\alpha_n)\}\exp(-D_1\alpha_n{}^2 t); \qquad (12)$$

$$\boldsymbol{D} \equiv \phi_1 \sin(R\alpha_n) + \phi_2 \cos(R\alpha_n);$$

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[†] 1 kcal=4184 J.

$$\phi_1 \equiv \{D_1R^{-1}(k_{d1}+k_{d2})-k_{a1}k_{d2}\}(\Gamma_\infty D_1R\alpha_n)^{-1} + \{R^{-1}(D_1R^{-1}-k_{a1}) - \Gamma_\infty{}^{-1}(k_{d1}+k_{d2})\}\alpha_n + D_1\alpha_n{}^3;$$

$$\phi_2 \equiv \{k_{a1}k_{d2}-D_1R^{-1}(k_{d1}+k_{d2})\}(\Gamma_\infty D_1)^{-1} - (D_1R^{-1}+k_{a1})\alpha_n{}^2;$$

$$\xi_i \equiv \{k_{a1}(c_{10}+D_1\alpha_n{}^2I_{1,i})-k_{d1}\theta_0\}\alpha_n - \{k_{a1}k_{d2}(c_{10}+D_1\alpha_n{}^2I_{1,i})-k_{a2}k_{d1}(c_{2\omega}+D_1\alpha_n{}^2I_{2,i})\}(\Gamma_\infty D_1\alpha_n)^{-1};$$

$$\zeta_{1,i} \equiv -(D_1\alpha_n)^{-1}\{D_1R^{-1}[k_{a1}(c_{10}+D_1\alpha_n{}^2I_{1,i})-k_{d1}\theta_0] - (k_{a1}-D_1R^{-1})[k_{a2}(c_{2\omega}+D_1\alpha_n{}^2I_{2,i})-k_{d2}\theta_0]\};$$

$$\mathrm{i}_{2,i} \equiv k_{a1}(c_{10}+D_1\alpha_n{}^2I_{1,i}) - k_{d1}\theta_0 + k_{a2}(c_{2\omega}+D_1\alpha_n{}^2I_{2,i}) - k_{d2}\theta_0;$$

$$I_{1,i+1} \equiv \frac{1}{2\pi\mathrm{i}}\int_{\sigma_1-\mathrm{i}\infty}^{\sigma_1+\mathrm{i}\infty}\{\bar{c}_{1,i}(\sigma)\}_{r=R}\bar{\theta}_{,i}(-D_1\alpha_n{}^2-\sigma)\mathrm{d}\sigma;$$

$$I_{2,i+1} \equiv \frac{1}{2\pi\mathrm{i}}\,c_{2\omega}\int_{\sigma_2-\mathrm{i}\infty}^{\sigma_2+\mathrm{i}\infty}\sigma^{-1}\bar{\theta}_{,i}(-D_1\alpha_n{}^2-\sigma)\mathrm{d}\sigma,$$

where the subscript $i$ designates including perturbation[11] to the $i$th term, provided $I_{1,0}=I_{2,0}=0$; $\bar{c}_1(p)$ and $\bar{\theta}(p)$ are the image functions corresponding to $c_1(t)$ and $\theta(t)$ respectively; here, $p$ is the conversion parameter of the Laplace transformation; $\pm\alpha_n$ are the roots (generally complex) of $\alpha$ in the next equation:

$$a_1\sin(R\alpha) + a_2\cos(R\alpha) = 0; \tag{13}$$

$$a_1 \equiv \{D_1R^{-1}(k_{d1}+k_{d2})-k_{a1}k_{d2}\} \times(\Gamma_\infty\alpha)^{-1}-(D_1R^{-1}-k_{a1})D_1\alpha;$$

$$a_2 \equiv D_1{}^2\alpha^2 - \Gamma_\infty{}^{-1}D_1(k_{d1}+k_{d2}).$$

The amount of solute in the sphere of Phase 1 on the condition that $(R_2-R_1)\rightarrow 0$ is represented by

$$q = 4\pi\int_0^R c_1{}^*r^2\mathrm{d}r$$

$$= (4/3)\pi R^3(k_{a1}k_{d2})^{-1}k_{a2}k_{d1}c_{2\omega} + 8\pi\sum_{n=1}^{\infty}(\alpha_n\boldsymbol{D})^{-1}\xi^* \times\{\alpha_n{}^{-1}\sin(R\alpha_n)-R\cos(R\alpha_n)\}\exp(-D_1\alpha_n{}^2t), \tag{14}$$

where the superscript* indicates the convergence in the progress of the perturbation.

Let us consider a stirred vessel with a certain volume, $V$, which is filled with Phase 1 (dispersed) and Phase 2 (continuous), with liquids of Phase 1 and Phase 2 constantly flowing in and out at the volumetrical rates of $F_1$ and $F_2$ respectively; these liquids (solvents) are immiscible and dissolved a solute in the initial concentrations of $c_{10}$ and $c_{20}$ respectively.

We calculate the concentration, $c_{2\omega}$, of the solute in Phase 2 (continuous) in the steady state; the dispersed particles are taken to be spheres of complete mixing,[12] and the distribution of the particle-diameters as well as the coalescence and fission of particles are disregarded for the sake of simplification.

The transfer rate of the solute from a sphere of Phase 1 to Phase 2 that is continuous (we use Eq. 14) is approximately given as

$$v = -\mathrm{d}q/\mathrm{d}t = 8\pi D_1\sum_{n=1}^{\infty}\boldsymbol{D}^{-1}\xi^*\{\sin(R\alpha_n)-R\alpha_n\cos(R\alpha_n)\} \times\exp(-D_1\alpha_n{}^2t).$$

The probability of the residence of a particle in the vessel (for complete mixing) may be represented as $Z=\exp(-Ft/V)$, where $F=F_1+F_2$; the probability density of the residence time is given by

$$f(t)=\mathrm{d}(1-Z)/\mathrm{d}t=(F/V)\exp(-Ft/V);$$

so the average rate of transfer may be expressed as

$$\bar{v} = \int_0^\infty vf(t)\mathrm{d}t = 8\pi D_1(F/V)\sum_{n=1}^{\infty}\boldsymbol{D}^{-1}\xi^*\{D_1\alpha_n{}^2+(F/V)\}^{-1} \times\{\sin(R\alpha_n)-R\alpha_n\cos(R\alpha_n)\}.$$

Considering the mass-balance, we obtain this relation: $\bar{v}nV=(c_{2\omega}-c_{20})F_2$, where $n$ is the number of particles per unit volume in the vessel, and after rearranging the relation, we may obtain a representation (for $\theta_0=0$) of the concentration sought as

$$c_{2\omega} = \{c_{20}+6D_1(R^3\gamma)^{-1}\sum_{n=1}^{\infty}[\psi_1(\alpha_n)+D_1\alpha_n{}^2I_2{}^*\psi_2(\alpha_n)]\} \times\{1-6D_1(R^3\gamma)^{-1}\sum_{n=1}^{\infty}\psi_2(\alpha_n)\}^{-1}; \tag{15}$$

$$\psi_1(\alpha_n) \equiv k_{a1}(c_{10}+D_1\alpha_n{}^2I_1{}^*)(\Gamma_\infty D_1\alpha_n{}^2-k_{d2})\Delta;$$

$$\psi_2(\alpha_n) \equiv k_{a2}k_{d1}\Delta; \quad \gamma \equiv F_2/F_1;$$

$$\Delta \equiv \{\alpha_n{}^{-1}\sin(R\alpha_n)-R\cos(R\alpha_n)\}\{\boldsymbol{D}[D_1\alpha_n{}^2+(F/V)]\}^{-1}.$$

## Some Computational Results

Figure 1 shows the time-dependences of the amount of solute in a sphere (where $q_\infty$ is the value in a transfer-equilibrium), with hypothetical values given to the parameters in Eq. 14; Curve a, in the case of an insignificant interfacial resistance ($\Delta F^{\ddagger}{}_{di}\approx 4$ kcal/mol), and Curve b (where $k_1=(5/6)\times10^{-5}$ cm/s; see Appendix), in the case of a significant interfacial resistance ($\Delta F^{\ddagger}{}_{di}\approx$

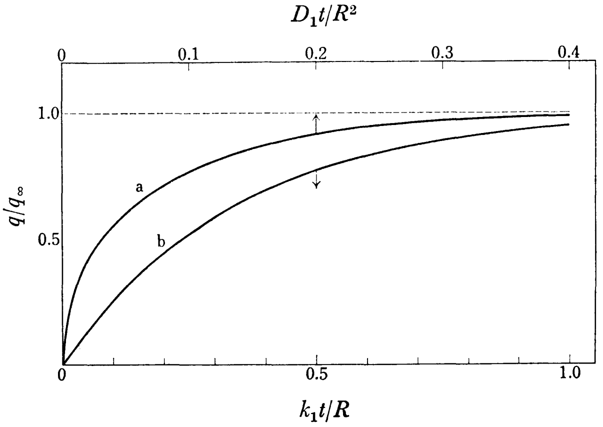

Fig. 1. Change in the amount of solute in a sphere. $D_1=10^{-5}$—$10^{-3}$ cm²/s; $R=1$—0.01 mm.

| Curve | a | b[a] |
|---|---|---|
| $\Gamma_\infty$/mol m$^{-2}$ | $7\times10^{-6}$ | $7\times10^{-6}$ |
| $k_{d1}$/mol cm$^{-2}$ s$^{-1}$ | 1 | 1 (5)$\times10^{-9}$ |
| $k_{d2}$/mol cm$^{-2}$ s$^{-1}$ | 1 | 5 (1)$\times10^{-9}$ |
| $k_{a1}$/cm s$^{-1}$ | $10^4$ | 1 (5)$\times10^{-5}$ |
| $k_{a2}$/cm s$^{-1}$ | $10^1$ | 5 (1)$\times10^{-5}$ |
| $c_{2\omega}$/mol m$^{-3}$ | 1 | 1 |
| $c_{10}$/mol m$^{-3}$ | 0 | 0 |
| $\theta_0$ | 0 | 0 |

a) The values of $k_{d1}$, $k_{d2}$, $k_{a1}$, and $k_{a2}$ substituted all the figures in the parentheses for ones on the left of the parentheses were also examined.

16 kcal/mol);[5,7] here, $\Delta F^{\neq}_{di}$ is the activation free energy of desorption from the interface to the $i$th phase; the diffusion coefficient, $D_1$, was changed at intervals from $10^{-5}$ to $10^{-3}$ cm²/s, and the radius of the sphere, $R$, from 1 to 0.01 mm, in both cases.

The values of the rate constants of adsorption and desorption were given by the following formulas:[1]

$$k_{ai} = \lambda_i(\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta F^{\neq}_{ai}/\boldsymbol{R}T);$$

$$k_{di} = \Gamma_\infty(\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta F^{\neq}_{di}/\boldsymbol{R}T);$$

$i=1$ and 2, where $\lambda_i(\approx 10$ Å††) is the length of the adsorption path from the boundary site of Phase $i$ to the interface; $\Delta F^{\neq}_{ai}$ is the activation free energy of adsorption from Phase $i$ to the interface; $\boldsymbol{k}$ is the Boltzmann constant; $\boldsymbol{h}$ is the Planck constant; $\boldsymbol{R}$ is the gas constant, and $T$ ($=300$ K) is the absolute temperature.

The procedure of calculation was as follows. Definite values were assigned to $D_1$, $\Gamma_\infty$, $R$, $k_{a1}$, $k_{d1}$, and $k_{d2}$ in Eq. 13, and the roots were found; although the roots, $\alpha_m$ ($m=1, 2, \cdots$), were generally complex, they were real[13] in those cases.

The values were assigned to $D_1$, $\Gamma_\infty$, $R$, $k_{a1}$, $k_{a2}$, $k_{d1}$, $k_{d2}$, $c_{10}$, $c_{2\omega}$, $\theta_0$, and $\alpha_n$'s ($n\leq 20$ usually suffices for convergence) in Eq. 14, and the amount of solute in the sphere, $q$, was computed as a function of the time, $t$. In those cases, $\theta\approx 0.005\ll 1$, and the $q$ value was computed approximately by the zero perturbation (substitute $c_{1,0}$ and $\xi_0$ for $c_1{}^*$ and $\xi^*$ in Eq. 14 respectively; see also Eqs. 4 and 5).

The computational results fell closely near the curves, a and b, in Fig. 1, in agreement with the values on the curves to the third decimal-digit. This means that, in the above ranges of conditions, the $q$ value may be expressed approximately by the following sublimate relations in the cases of "an insignificant interfacial resistance" and of "a significant interfacial resistance" respectively:

$$q/q_\infty = f_1(D_1t/R^2), \text{ and } q/q_\infty = f_2(t/R),$$

where $f_1$ and $f_2$ designate functional relations.

The a curve well fits the next equation[14] of no interfacial resistance:

$$q/q_\infty = 6\pi^{-1/2}(D_1t)^{1/2}/R - 3D_1t/R^2 + \{12(D_1t)^{1/2}/R\} \times \sum_{n=1}^{\infty}\mathrm{ierfc}\{nR/(D_1t)^{1/2}\}. \quad (16)$$

This may be an expression of the functional relation, $f_1$.

The b curve indicates that the $q$ value in the case of "a significant interfacial resistance" ($\Delta F^{\neq}_{di}\approx 16$ kcal/mol) has practically no relation to the diffusion coefficient, $D_1$. This means that the diffusion process in bulk phases cannot be the rate-determining step under these conditions (see Appendix).

The a, b, and c curves in Fig. 2 predict the changes in the concentration of solute ($c_{2\omega}$) in the continuous phase (aqueous) as functions of $F/V$, as calculated by means of Eq. 15 (of $I_1{}^*=I_2{}^*=0$) when a 1 mol/m³ ($c_{20}$) aqueous solution of butylamine and a solvent, benzene, was allowed to flow into a stirred vessel in the flow ratio $\gamma=5$ (water/benzene) at 50 °C, and the spherical particles of the dispersed phase had radii ($R$) of exactly 1, 0.1, and 0.01 mm respectively; the other parameters were set as follows: $D_1=3.206\times 10^{-5}$ cm²/s;[15] $\Gamma_\infty=6.83\times 10^{-6}$ mol/m²;[18] $k_{a1}=7.85\times 10^3$ cm/s;[7] $k_{a2}=1.089\times 10^{-4}$ cm/s;[7] $k_{d1}=1$ mol/cm² s;[7] $k_{d2}=5\times 10^{-9}$ mol/cm² s;[7] $c_{10}=\theta_0=0$.

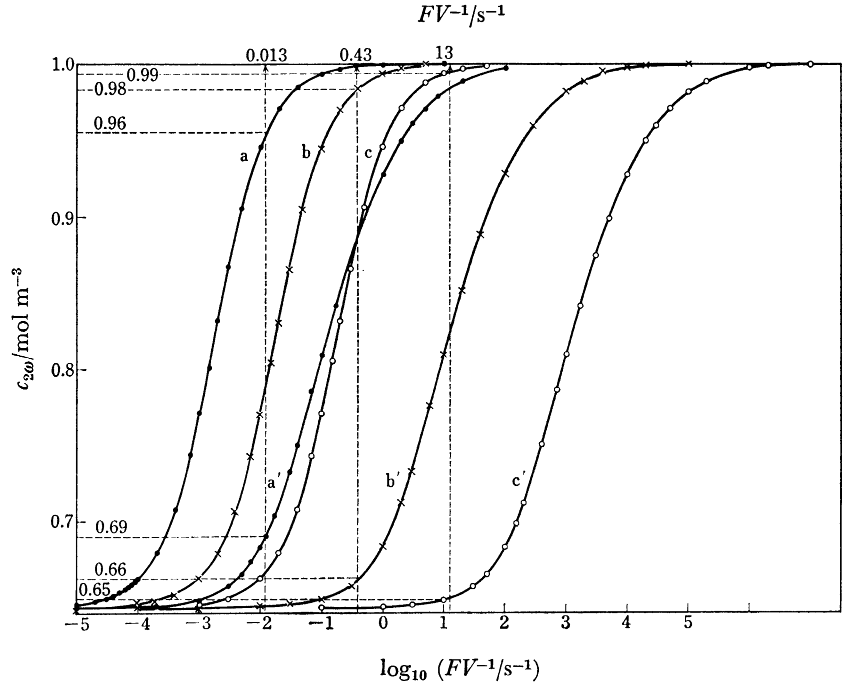

Fig. 2. $F/V$ Dependence of $c_{2\omega}$. Sample: 1 mol/m³ aqueous solution of butylamine and benzene; $\gamma$ (water/benzene)$=5$; temperature$=50$ °C. a, a′: $R=1$ mm; b, b′: $R=0.1$ mm; c, c′: $R=0.01$ mm.

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†† 1 Å$=10^{-10}$ m.

The a′, b′, and c′ curves in Fig. 2 indicate the relation supposing the interfacial resistance was negligible; the two parameters were reset as follows: $k_{a2}=2.178\times10^4$ cm/s and $k_{d2}=1$ mol/cm$^2$ s.

An examination of the magnitude of the interfacial resistance may be effectively made under the given conditions provided the $F/V$ ratios are set as 0.013, 0.43, and 13 s$^{-1}$ in experiments with $R=1$, 0.1, and 0.01 mm respectively: If the resistance is significant ($\Delta F^{\neq}{}_{d2}=18$ kcal/mol), the $c_{2\infty}$ values are determined to be 0.96, 0.98, and 0.99 mol/m$^3$ respectively, while if the resistance be negligible, the $c_{2\infty}$ values are determined to be lower[19] than 0.69, 0.66, and 0.65 mol/m$^3$ respectively.

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## Appendix

When the transfer resistance in the bulk phases is negligible as compared with the interfacial resistance, the next equation may be derived as a specific case of Eq. 14, neglecting also the variation in the amount of adsorption on the interface:[1,3]

$$q = q_\infty - (q_\infty - q_0)\exp(-3k_1t/R); \qquad (17)$$
$$k_1 \equiv k_{a1}\{1+(k_{d1}/k_{d2})\}^{-1},$$

where $q_0$ is the initial amount of solute in a sphere and $k_1$ is the effective rate constant for transferring through the interface from Phase 1 to Phase 2. Equation 15 may then be simplified as follows:

$$c_{2\infty} = (c_{10}+c_{20}H)(K+H)^{-1}; \qquad (18)$$
$$H \equiv \gamma\{1+(R/3k_1)(F/V)\};\ K \equiv (k_{a1}k_{d2})^{-1}k_{a2}k_{d1}.$$

The computational values using these formulas also fit well the b curve in Fig. 1 and the a, b, and c curves in Fig. 2.

Figure 3 shows the limits of the application of Eqs. 16 and 17 to pairs of values of $k_1$ and $R$ at $D_1=10^{-5}$ cm$^2$/s. The lines indicating the limits were drawn on the assumption that every pair of $k_1$ and $R$ on the lines made the $q$ value computed by means of the specific equations (Eq. 16 or 17) deviate from that computed by means of Eq. 14 exactly 5% at the time of $q/q_\infty$(Eq. 14)$=0.5$;[20] these lines should be considered to give a sort of standard, and the change in the time, $t$, as well as in the diffusion coefficient, $D_1$, transfers the position of the 5% lines.

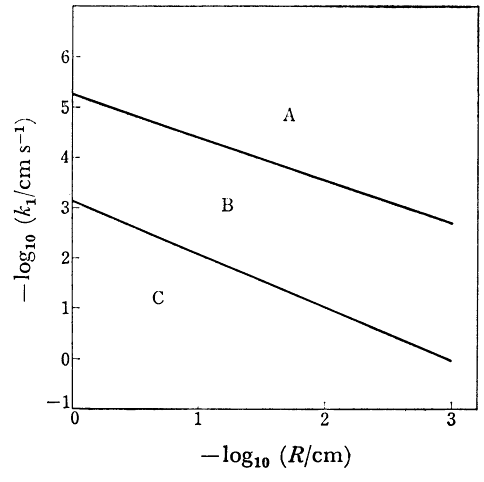

Fig. 3. Limits of application of the specific equations. $D_1=10^{-5}$ cm$^2$/s; $q/q_\infty=0.5$. A: Bulk-diffusional resistance is negligible (Eq. 17 is applicable). B: Neither bulk-diffusional nor interfacial resistance is negligible. C: Interfacial resistance is negligible (Eq. 16 is applicable).

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9) This treatment is almost the same as the linear diffusion through a plane interface treated before, and so the description will be abbreviated.
10) J. Crank, "The Mathematics of Diffusion," Clarendon Press, Oxford (1956), p. 84.
11) The calculation of $I_{1,i}$ and $I_{2,i}$ is easy, but somewhat lengthy, and so it is omitted here.
12) This means that the time-average of the local concentration of the solute tends to be constant in every part in the vessel because of the random change in the relative positions of the dispersed particles.
13) This is determined, for example, by the means described in Footnote 19 in the literature of Ref. 7.
14) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," 2nd ed, Clarendon Press, Oxford (1960), p. 234.
15) This was estimated by Wilke's method[16] from the literature.[17]
16) C. R. Wilke, *Chem. Eng. Progr.*, **45**, 218 (1949).
17) J. T. Davies and J. B. Wiggill, *Proc. R. Soc., London, Ser. A*, **255**, 277 (1960).
18) This is equivalent to the value of $B=24.3\times10^{-16}$ cm$^2$/molecule cited in the literature of Ref. 7.
19) It is considered that the apparent diffusion coefficient is greater than the value estimated because of agitations.
20) Change in the values of the rate constants of adsorption and desorption on condition that $k_1=$const, $k_{a1}/k_{d1}=$const, and $k_{a2}/k_{d2}=$const gives practically constant $q$'s computed by Eq. 14, agreeing to the third decimal-digit.